AD-A205 975

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REPORT DOCUMENTATION PAGE

DTIC FILE COPY

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release Distribution Unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) # 1	5. MONITORING ORGANIZATION REPORT NUMBER(S) N0014-87-K-0529
6a. NAME OF PERFORMING ORGANIZATION Rutgers-The State University of New Jersey 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. R. Schwartz
6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code) Code 3854 Naval Weapons Center China Lake, CA 93555
8a. NAME OF FUNDING / SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO / TASK NO. / WORK UNIT NO

DTIC ELECTE 10 MAR 1989 S E D

11. TITLE (Include Security Classification)

Mechanical Behavior of PMMA-Impregnated Silica Gels

12. PERSONAL AUTHOR(S)

B. Abramoff and L. C. Klein

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	1989 February 27	9

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

89 3 08 012

Office of Naval Research

Contract N00014-87-K-0529

Task No. 431a019

Technical Report No. 1

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

MECHANICAL BEHAVIOR OF PMMA-IMPREGNATED SILICA GELS

by

Bennet Abramoff and Lisa C. Klein

Prepared for Publication

in the

Proceedings of the Fourth International Conference on

Ultrastructure Processing of Ceramics, Glasses and Composites

Rutgers-The State University of New Jersey

Ceramics Department

P.O. Box 909

Piscataway, NJ 08855-0909

February 27, 1989

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"Mechanical Behavior of PMMA-Impregnated Silica Gels"

B. Abramoff and L. C. Klein
Rutgers-The State University of New Jersey
Ceramics Department
P.O. Box 909
Piscataway, NJ 08855-0909

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February 19-24, 1989
Tucson, AZ

Abstract

Silica xerogels have been prepared from tetraethyl orthosilicate with 50 volume percent open porosity. Methyl methacrylate monomer has been introduced into xerogel monoliths and polymerized with ultraviolet radiation. The fully infiltrated silica gel - PMMA composite has a bulk density of about 1.6 g/cm^3. The resulting composite is lightweight and optically transparent. Elastic constants have been determined with ultrasonics. Flexure strengths have been measured in 4-point bending. The flexure strength of the composite is over 100 MPa in comparison to 20 MPa for the silica xerogel. The composite is designed for use at or below room temperature.

Introduction

Only a handful of studies have reported mechanical properties of sol-gel processed silica. These include alcogels (1), aerogels (2,3), xerogels (4,5) and colloidal gels (6). For alcogels, aerogels and colloidal gels, Young's modulus and strength have been measured. For silica xerogels from silicon alkoxides, elastic constants and strength have been measured. A typical value for Young's modulus is about 10 GPa and a typical strength is 20 MPa (4). The elastic constants of xerogels are found to be sensitive to relative humidity. To lessen the sensitivity to moisture without increasing the weight substantially, it is possible to impregnate the xerogel with (poly) methylmethacrylate (PMMA) and, at the same time, maintain optical transparency (7).

Silica xerogel monoliths have been infiltrated with PMMA and other glassy polymers (7,8). Processing of the xerogels involved catalysis with HF and firing to 800°C. The resulting xerogels were 33% porous and had a median pore diameter of 10 nm. The porous gels were infiltrated with monomer solutions and polymerized in-situ. The resulting composites consisted of two fully percolating phases, a silica matrix and an organic polymer impregnant. The measured Young's modulus was about 30 GPa (8).

The silica/PMMA composite can be used to encapsulate electro-optically active organic compounds such as 2-methyl-4-nitroaniline (MNA). Electro-optical DC Kerr Effect and solid state deuteron NMR measurements were made (9). In comparison to conventional optical cells, silica/PMMA composites had better optical quality and retained dimensional stability to about 90°C. The composites were abrasion resistant and could be machined to complex shapes.

Following this concept, the question is whether or not it is possible to have a composite with a lower density and *finer texture* for improved toughness? Ideally, all processing should be at room temperature instead of at 800°C for heat treatment. Monolithic xerogels which are 50% porous with a median pore diameter of 2 nm (10) were used to prepare composites without high temperature treatment.

Experimental Techniques

Silica xerogels were prepared from a solution of tetraethylorthosilicate (TEOS), distilled deionized water and ethanol. Equal volumes of distilled TEOS and ethanol were used. The molar ratio of water: TEOS was 16 (10). The solution was catalyzed with 0.1 M HNO_3 and was stirred for 30 minutes. Polystyrene tubes were filled with 10 ml of the solution. Samples were gelled in an oven for 7 days at 50°C and then at 70°C for 10 days. Next, the tubes were uncovered and dried in lots of 100 at 50°C for 14 days. Xerogels were removed from the

tubes and dried 2 more days at 50°C. Finally, the gels were outgassed 24 hours at 250°C to remove physically adsorbed species.

A monomer solution of 1 g benzoyl peroxide (97%) catalyst per 100 ml MMA (methylmethacrylate, inhibited) was prepared (Aldrich Chemicals, Milwaukee, Wi). After outgassing, each xerogel was immediately immersed in a borosilicate vial containing 11 ml of the monomer solution (I). The solution was allowed to infiltrate for 2 hours and then the sealed vials were polymerized 7 days in a cabinet with longwave UV illumination (II). The cabinet had a UV intensity of about 2000 micro W/cm^2, a temperature 3°C above ambient, and a fan to dissipate heat from the vials. After polymerization, the vials were destructively removed and the PMMA surrounded composites were treated at 200°C in a mechanical convection oven for 30 minutes (III). This is a temperature about 100°C above the glass transition temperature of bulk PMMA and is also high enough to promote a moderate rate of depolymerization. Immediately after removal from the oven, the now rubbery and bloated PMMA shells were removed by hand to recover net shape composites (IV). These steps (I-IV) are shown schematically in Figure 1.

Density and porosity were measured using Archimedes method. Density was determined in freshly boiled deionized water. Before immersion in water, silica matrices were exposed to ambient conditions for 2 days to prevent explosion. The open porosity of the silica matrix was measured with methanol, ethanol, and MMA monomer solution. Five samples were measured for each test and immersion time with all solvents was 24 hr. Surface area, pore size distribution, and pore shape were measured using nitrogen sorption on the Omnisorp 360^{TM} (Omicron Technology, Berkeley Heights, NJ). After outgassing 24 hr at 250°C, monolithic xerogels were outgassed 2 hr at 250°C under vacuum in the unit before analysis.

Strength measurements were made by the four point flexure technique. The flexure fixture had a support span of 2.540 cm (1.000") and a load span of

1.270 cm (0.500"). A gear driven Instron materials testing machine with a 1000 lb load cell was used. Crosshead speeds were .05 cm/min (0.02"/min) for silica and silica/PMMA and 5.08 cm/min (2.0"/min) for PMMA. The rapid strain rate for PMMA was necessary to prevent elastic deformation. Silica samples were measured before and after outgassing. Composite samples were measured fresh, within 1 hour of recovery from the PMMA, and also after exposure to ambient conditions for 14 days. Water adsorption in PMMA was only on the order of .1% even after exposure. Sample test sets numbered 50 for silica and silica/PMMA and 20 for PMMA.

Elastic constants were measured with ultrasonic NDE. Transducers used in the pitch/catch mode for longitudinal and transverse wave velocities were 5 Mhz WC50-5 and 2Mhz SDB25-2 (Ultran Laboratories, State College, PA). For each test, five samples were measured. Materials were ground dry on two sides to produce test samples of about 4 mm thickness. Silica samples were measured within 3 minutes of outgassing and with less than .5% water adsorption. Composites were measured fresh. Young's modulus, E, and shear modulus, G, were calculated directly from the longitudinal wave velocities, v_L, transverse wave velocities, v_T, and bulk densities, p, according to:

$$E = [3pv_L^2 - 4pv_T^2]/[(v_L/v_T)^2 - 1] \quad (1)$$

$$G = pv_T^2 \quad (2)$$

Poisson's ratio, n, and bulk modulus, K, were then determined from relations:

$$n = E/2G - 1 \quad (3)$$

$$K = E/3(1 - 2n) \quad (4)$$

Results

Silica samples were roughly cylindrical in shape with some tapering from top to bottom. The diameter at the center of the outgassed matrixes and composites was 5.60 mm and the length was about 33 mm. Linear shrinkage of the gel due to outgassing was 2.2%. Nitrogen adsorption and desorption yielded information on pore size and texture. The surface area of the matrix was 900 m^2/g. Porosity was almost completely microporous (less than 2.0 nm in diameter) and cylindrical in shape.

Table 1 summarizes physical characteristics. Listed are bulk densities and open porosities. Assuming no closed porosity to methanol or ethanol gives a skeletal density about 2.27 g/cm^3. The open porosity in MMA was 52.5% compared to 53.4% in methanol and ethanol. The composite was 94% theoretical density and 8.5% calculated total porosity. The total weight gain during infiltration followed by polymerization was 50%.

Table 2 lists elastic properties of the materials. Included are the longitudinal and transverse wave velocities, Young's modulus, shear modulus, bulk modulus and Poisson's ratio.

Figure 2 shows the strength distributions of each set of 50 samples as represented by the two parameter Weibull analysis (11). Values of mean strength, Weibull modulus and correlation coefficient are listed in Table 3. Water adsorption for silica was 26% during the testing at 50% relative humidity. Water adsorption for aged composites was 1.2% during the testing at 20% relative humidity. Outgassing of the xerogels led to a small increase in strength and a widening of the distribution. Aging of the composite led to a slight decrease in strength.

Discussion

The heat treatment at 200°C served two purposes. First, the treatment

allowed extraction of net shape composites. Additionally, the treatment relieved some stresses that developed from expansion of PMMA during the last stages of polymerization. This expansion of the thick shell was enough to break the borosilicate vials after a few days of polymerization.

Although composites were lightweight and optically transparent, they were only 94% dense. Attainment of 100% theoretical density was limited primarily by resistance to infiltration during polymerization. In bulk, MMA densifies from .94 g/cm^3 to 1.18 g/cm^3 during polymerization. However, as the average molecular weight of the monomer solution increases during polymerization it becomes increasingly difficult for the monomers to infiltrate the matrix. Because of the very fine size of the silica microporosity, about 1% of the matrix volume is not impregnable by even the initial monomer solution. Previously, it was determined that the PMMA in the composite contains a larger concentration of residual MMA than bulk PMMA (9).

Outgassing of the silica xerogels tended to increase strength slightly and widen the distribution. The strengthening may be attributed to some condensation of hydroxyls on the silica surface and the widening of the distribution is likely due to some damage to the surface. Although the use of different strain rates and surface conditions prevents direct comparison, it appears that the strength of the composites is similar to bulk PMMA, with a somewhat wider distribution in strengths for the composites. This indicates preexisting matrix flaws are not healed by impregnation or that new flaws are introduced by impregnation. Adsorption of water may decrease the strength of composites slightly due to corrosion of siloxane bonds of the silica matrix. Nevertheless, the water adsorption of the composites is negligible compared to adsorption for the xerogel without impregnation. The impregnated xerogel offers mechanical stability for longer exposure times.

Acknowledgement

The financial support of the Office of Naval Research under Contract N00014-87-K-0529 is greatly appreciated.

References

1. S. A. Pardenek, J. W. Fleming and L. C. Klein, M.R.S., Vol. 88, Better Ceramics through Chemistry III, eds. C. J. Brinker, D. E. Clark, and D. R. Ulrich (Pittsburgh, PA, 1988) p. 73.

2. T. Woignier, J. Pelous, J. Phalippou, R. Vacher and E. Courtens, J. Non-Cryst. Solids, 95/96, (1987) 1197.

3. T. Woignier and J. Phalippou, J. Non-Cryst. Solids, 100 (1988) 404.

4. M. J. Murtagh, E. K. Graham and C. G. Pantano, J. Am. Ceram. Soc., 69 (1986) 775.

5. S. C. Park and L. L. Hench, Science of Ceramic Chemical Processing, eds. L. L. Hench and D. R. Ulrich (Wiley, NY 1986) p. 168.

6. D. Ashkin, R. A. Haber and J. B. Wachtman, J. Am. Ceram. Soc. (1989) to appear.

7. E. J. A. Pope and J. D. Mackenzie, M.R.S. Vol. 73, Better Ceramics through Chemistry II, eds. C. J. Brinker, D. E. Clark and D. R. Ulrich (Pittsburgh, PA, 1986) p. 809.

8. E. J. A. Pope and J. D. Mackenzie, 32nd International SAMPE Symposium (1987) 760.

9. T. M. Che, R. V. Carney, G. Khanarian, R. A. Keosiuan and M. Borzo, J. Non-Cryst. Solids, 102 (1988) 280.

10. L. C. Klein, T. A. Gallo and G. J. Garvey, J. Non-Cryst. Solids, 63 (1984) 23.

11. S. B. Batdorf, Fracture Mechanics of Ceramics: Vol. 3 Flaws and Testing, eds. R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1978) p. 1.

List of Figures

Table 1: Physical Characteristics

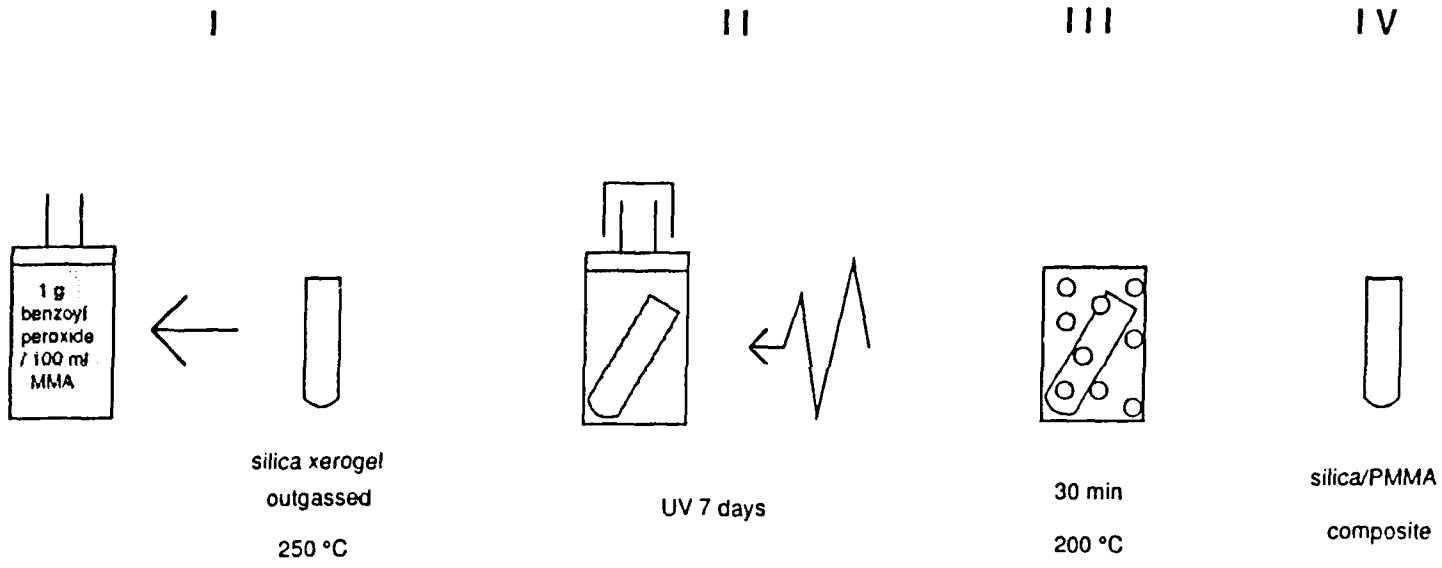
	Bulk Density g/cm^3	Porosity %
Silica xerogel	1.06	53.4%
Silica/PMMA	1.59	8.5%
PMMA	1.18	---

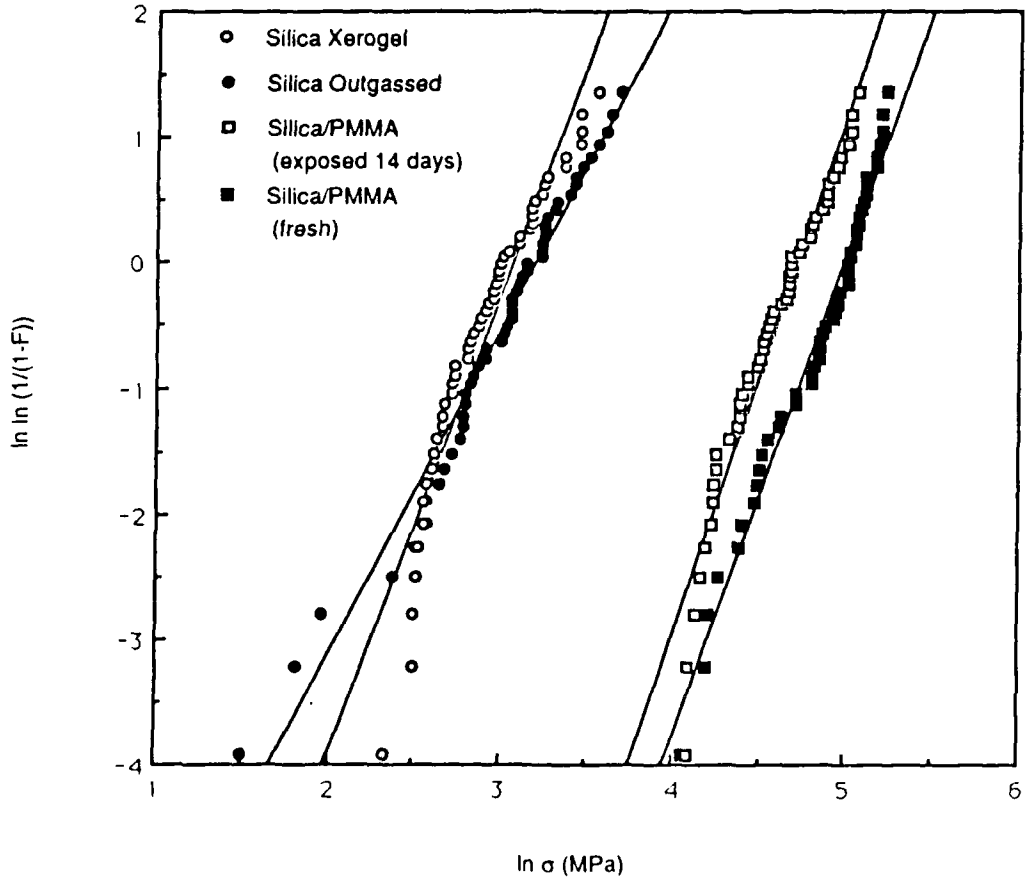
Table 2: Elastic Properties

	v_L km/sec	v_t km/sec	E GPA	G GPA	K GPA	n
Silica xerogel	2.25	1.40	4.9	2.1	2.6	.18
Silica/PMMA	3.19	1.87	14.0	5.6	8.9	.24
PMMA	2.69	1.37	5.8	2.2	5.6	.33

Table 3: Strengths

	Strength MPA	Weibull Modulus	R^2
Silica xerogel	19.3	3.7	.91
Silica xerogel (outgassed)	21.6	2.6	.97
Silica/PMMA (fresh)	132	3.9	.98
Silica/PMMA (exposed 14 days)	102	4.1	.95
PMMA	119	8.9	.97


I
II
III
IV
1 g benzoyl peroxide / 100 ml MMA
silica xerogel
outgassed
250 °C
UV 7 days
30 min
200 °C
silica/PMMA
composite


Silica Xerogel
Silica Outgassed
Silica/PMMA
(exposed 14 days)
Silica/PMMA
(fresh)
ln ln (1/(1-F))
ln σ (MPa)
2
1
0
-1
-2
-3
-4
1
2
3
4
5
6